A Born-Oppenheimer photolysis model of N_2O fractionation

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[1] The isotopically light N_2O produced by microbial activity is thought to be balanced by the return of heavy stratospheric nitrous oxide. The *Yung and Miller* [1997] method that first explained these trends yields photolytic fractionation factors ~half those observed by experiment or predicted quantum mechanically, however. To address these issues, we present here a Born-Oppenheimer photolysis model that uses only commonly available spectroscopic data. The predicted fractionations quantitatively reproduce laboratory data, and have been incorporated into zonally averaged atmospheric simulations. Like *McLinden et al.* [2003], who employ a three-dimensional chemical transport model with cross sections scaled to match laboratory data, we find excellent agreement between predictions and stratospheric measurements; additional processes that contribute to the mass independent anomaly in N_2O can only account for a fraction of its global budget. *INDEX TERMS:* 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 0322 Atmospheric Composition and Structure: Constituent sources and sinks.
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[2] Nitrous oxide, N_2O, is a central component of the global nitrogen biogeochemical cycle. Produced primarily by terrestrial and marine microbial communities as a by-product of nitrification and denitrification reactions, N_2O is a potent greenhouse gas and the principal natural driver of stratospheric NO_x chemical cycles and ozone loss. The atmospheric concentration of nitrous oxide is increasing at ~0.25%/yr [*Houghton et al.*, 2001]. Accordingly, N_2O is one of the trace gases regulated by the 1997 Kyoto Protocol. Unlike truly anthropogenic compounds such as SF_6, however, N_2O mitigation efforts necessarily involve consideration of the complex processes that govern biological and geochemical cycling in the near-surface environment.

[3] Characterization of the isotopic composition of biogenic trace gases can provide important constraints on their sources and atmospheric processing. Initial work on the ^{15}N and ^{18}O content of atmospheric N_2O [*Kim and Craig*, 1993] demonstrated that the stratospheric return flux must be enriched in these nuclei in order counter the isotopically light nitrous oxide produced biologically. In the "standard" model of stratospheric chemistry [*DeMore et al.*, 1997] the dominant reactions involving N_2O are photolysis, or which accounts for ~90% of the observed loss; the remaining "photo-oxidation" channel involves the reaction of N_2O with $O(^1D)$ to produce either two NO molecules or $N_2 + O_2$. In response to laboratory studies which revealed that neither photolysis near 185 nm nor the reaction with $O(^1D)$ produce sufficiently fractionated products [*Johnston et al.*, 1995], and to the discovery of a "mass independent" oxygen isotope fractionation [MIF, *Cliff and Thiemens*, 1997], a number of more exotic means of producing stratospheric N_2O have been proposed [*Prasad and Zipf*, 2000].

[4] Studies of a larger suite of samples revealed a fractionation pattern consistent with a single stage loss process [*Rahn and Wahlen*, 1997], leading *Yung and Miller* [1997] (YM97) to propose a wavelength-dependent photolytic fractionation for N_2O. This theory, based on the differences in zero-point energy (ZPE) of various isotopologues and the fact that the stratospheric photolysis of N_2O occurs mainly from 195–205 nm and not at the cross section peak, accounted for the pattern of the available measurements and predicted isotopomer specific fractionation in $^{14}N^{15}N^{16}O$ versus $^{15}N^{14}N^{16}O$.

[5] A flurry of laboratory [*Rahn et al.*, 1998; *Umemoto*, 1999; *Röckmann et al.*, 2000; *Turatti et al.*, 2000; *Zhang et al.*, 2000; *Kaiser et al.*, 2002, 2003] and atmospheric [*Rahn and Wahlen*, 1997; *Yoshida and Toyoda*, 2000; *Griffith et al.*, 2000; *Röckmann et al.*, 2001a, 2001b; *Toyoda et al.*, 2001] tests of YM97, including the analysis of position-specific ^{15}N fractionation and $^{16,17,18}O$ MIF, have confirmed that photolytically-induced isotopic fractionation is a process of widespread importance in planetary atmospheres. Nevertheless, the laboratory fractionation values are nearly twice those predicted by YM97, and $^{16,17,18}O$ are mass-dependent at 193 nm to within experimental error. Do these discrepancies reflect a fundamental lack of understanding of atmospheric chemistry?

[6] In YM97, the isotopic spectra are assumed to be identical save for small ZPE-induced wavelength shifts. Heavier isotopologue cross sections are blue-shifted, and so lead to slower photolysis at long wavelengths. Fractionation values are negligible near the peak, and switch signs at shorter wavelengths. These assumptions are not strictly valid, and in recent *ab initio* calculations *Johnson et al.* [2001] have convincingly shown that the fractionation values are indeed likely to be much larger than predicted by YM97. Furthermore, recent atmospheric simulations using the *ab initio* cross sections [*McLinden et al.*, 2003] yield good agreement with atmospheric measurements.

[7] In order to place these disagreements into a solid physical context and to enable wider applications, we present here an analytical approach to the isotopic dependence of photolysis that, unlike *ab initio* methods, enables predictions to be made using only data commonly available for trace gases, namely the major photolysis cross sections and the ground state isotope-specific spectroscopic constants, yet which captures faithfully the complex dynamics present in

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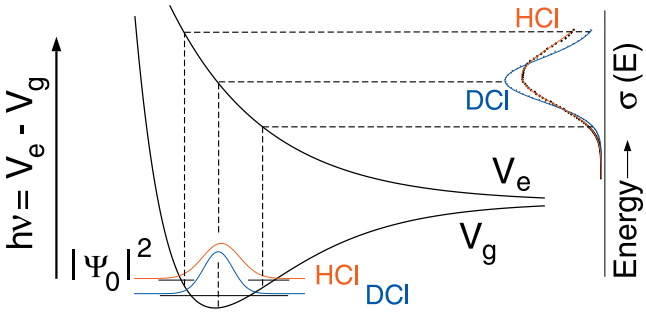

Figure 1. A schematic diagram of the direct photodissociation process. In the Born-Oppenheimer approximation, the photon energy is $h\nu = V_e - V_g$, independent of isotopic substitution. The analytical fits to the HCl/DCl cross sections yield the ground state wavefunctions. The ZPE difference is exaggerated for clarity.

polyatomic systems such as N_2O. For simplicity, we first consider the diatomic case before turning to N_2O photolysis in the laboratory and stratosphere.

[8] Figure 1 presents an overview of direct photodissociation for diatomic molecules. Within the Born-Oppenheimer approximation, the potential curves are independent of isotopic substitution. The absorption of a photon conserves the position *and* momentum of the nuclei, and so the transitions should be drawn from potential to potential, and *not* from the eigenstate energy to V_e as is shown in many texts [c.f. Figure 1; *Mulliken*, 1971; *Schinke*, 1993]. The ZPE of the ground vibrational state is isotopically sensitive, however, since ZPE = $\bar{h}\omega_0/2$ and $\omega_0 = \sqrt{k/\mu}$, where ω_0 is the vibrational frequency, k the ground state potential curvature evaluated at the bond length R_0, and $\mu = M_1M_2/(M_1 + M_2)$ the reduced mass. In the reflection approximation, the excited state potential is assumed to be linear and the dipole matrix element D constant over the bond length changes experienced in the ground state. In this limit, the probability distribution is directly mapped onto the energy axis to produce cross sections given by $\sigma \propto \nu D^2|\Psi|^2$ cm^{-2}.

[9] At first blush, would seem to leave photodissociation isotopically insensitive. Due to the anharmonic ground state potential, however, the vibrationally-averaged bond length shrinks as the reduced mass increases, resulting in the blue shift cited by YM97 for heavier isotopologues. While the shift is proportional to the ZPE, its magnitude depends on the geometry changes and especially on the slope of the upper state - steeper slopes give larger shifts and broader absorption spectra for a fixed ground state potential.

[10] More importantly, the shape of the wavefunction, or $|\Psi(R)|^2 = (\alpha/\pi)^{1/2}e^{-\alpha(R-R_0)^2}$, is quite sensitive to isotopic substitution. For harmonic oscillators, the ratio of the two "width" parameters for the major (light = L) and minor (heavy = H) isotopologues is $[\alpha(L)/\alpha(H)] = [\text{ZPE}\ (H)/\text{ZPE}\ (L)]^{1/2}$. Heavier isotopologues should therefore possess narrower photodissociation spectra with higher peak cross sections (c.f. Figure 1). Numerically, for an upper state slope of V_e', the corresponding width parameter of the absorption spectrum is $\beta = \alpha/(V_e')^2$. For neutrals, the relationship $D(R) \rightarrow 0$ as $R \rightarrow \infty$ and the curvature in actual repulsive potentials enhance the blue wing absorption. Linear variations in $D(R)$ and a quadratic $V_e(R)$ modify the spectral shape by an *isotope independent* polynomial of order five that decreases monotonically with R, and, as Figure 1 shows, fits of 5th-order polynomial-weighted Gaussians to the HCl/DCl cross sections [*Bahou et al.*, 2001] reproduce the data to within experimental error.

[11] For triatomics such as O_3 and N_2O, the diatomic Born-Oppenheimer model can be extended to yield $\beta = (V_e'(R)^2/\alpha_R + V_e'\,(r)^2/\alpha_r + V_e'\,(\theta)^2/\alpha_\theta)^{-1}$, where r and R are two bond distances (N-N and the O-(N-N) center-of-mass difference for N_2O), and θ the angle between them [*Schinke*, 1993]. Given the isotope-specific vibrational frequencies, the calculation of the relevant α values, and thereby the spectra, follows the diatomic example.

[12] In laboratory experiments, the photolytic fractionation, expressed in the per mil notation commonly used in geochemistry, should follow that of Rayleigh distillation, or $\epsilon(\text{permil}) = 1000\left[\frac{\sigma(H)}{\sigma(L)} - 1\right]$, where $\sigma(L)$ is the cross section of the major isotopologue and $\sigma(H)$ that of the substituted species. Inserting the expressions above yields

$$\epsilon(\nu) = 1000\left(\left[\frac{\beta(L)}{\beta(H)}\right]^{1/2} e^{-\left[\beta(L)[\nu-\nu_0(L)]^2-\beta(H)[\nu-\nu_0(H)]^2\right]} - 1\right), \quad (1)$$

where $\nu_0(L)$ and $\nu_0(H)$ are the cross section maxima. In YM97, $\beta(L) = \beta(H)$ and $\nu_0(H) - \nu_0(L) = \Delta\text{ZPE}$, so that $\varepsilon \sim -2000\ \beta(L)\ \Delta\text{ZPE}\ [\nu - \nu_0(L)]$, for small ΔZPE. Thus, the YM97 fractionation is linear and negative at long wavelengths while positive to the blue, but the general expression is in fact a ratio of Gaussians (Figure 2).

[13] As Figures 1 and 2 show, the isotopic cross sections of HCl and O_3 [*Parisse et al.*, 1996] do indeed have different shapes. An analytical prediction of the O_3 ratios using equation (2) and only the $^{16}O_3$ data along with the ZPE and α factors inferred from the vibrational frequencies [*Flaud and Bacis*, 1998] is seen to reproduce the fractionation experiment, and demonstrates that both the shift in the

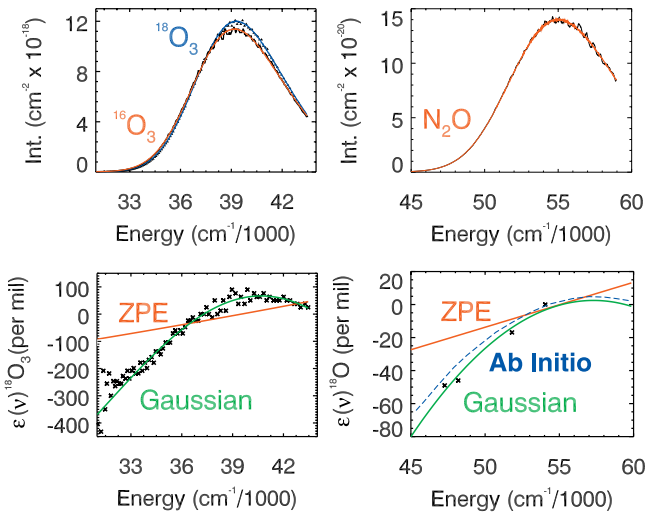

Figure 2. Absorption cross sections and fractionation factors for $O_3/^{18}O_3$ (left) and $N_2O/N_2{}^{18}O$ (right). The cross sections are fit using polynomial-weighted Gaussians, while in the lowermost panels the straight line shows the fractionation predicted by YM97 (ZPE). Solid curves depict the analytical fits outlined here. Data are plotted as crosses. For $N_2O/N_2{}^{18}O$, the dashed curve, shows the *ab initio* predictions of *Johnson et al.* [2001].

cross sections with isotopic substitution and the change in the wavefunction shape are important.

[14] Is this effect large enough to account for the differences observed between the predictions of YM97 and the many laboratory photolysis experiments on nitrous oxide? The dissociation of N_2O is known to involve complex dipole moment and potential energy surfaces (PESs) that result from an avoided crossing [*Johnson et al.*, 2001]. In what follows, we have found that linear treatments, in which case $V_e'(\theta) = 0$, provide the best fits to the available data. As before, isotopically substituted vibrational frequencies [YM97] are used to calculate the relevant α values.

[15] The cross sections of N_2O are known to be temperature dependent thanks to the improved Franck-Condon factors of vibrationally excited bending states with the dissociating surface(s). By combining the spectra of N_2O versus temperature [*Selwyn and Johnston*, 1981; *Merienne et al.*, 1990], we have separated the ground and excited bending state cross sections [c.f. *Selwyn and Johnston*, 1981]. For simplicity, we assume the same temperature dependence for all isotopologues.

[16] At lower stratospheric temperatures, dissociation from the vibrational ground state dominates N_2O photolysis. Due to the smooth nature of the spectrum, the isotopic blue shifts are difficult to measure, but the vibrational structure present at 295 K indicates offsets close to those predicted from the ΔZPE values, as is true for O_3. At $\lambda \gtrsim 200$ nm, the blue shift and wavefunction narrowing contributions are similar, and yield fractionations very close to those seen in the laboratory, as Figure 2 shows for $N_2{}^{18}O/N_2O$ (similarly good results are found for all of the remaining N_2O isotopologues). Small (<2%) variations in D, consistent with the *ab initio* dipole moment surface [*Johnson et al.*, 2001], are needed to reproduce the near zero fractionation at 185 nm. Due to the continuum nature of the fits the vibrational structure observed in the laboratory room temperature spectra is not reproduced [c.f. Figure 2; *Selwyn and Johnston*, 1981; *Kaiser et al.*, 2003], but since the stratospheric photolysis occurs over large wavelength intervals this does not introduce serious error.

[17] In a recent three-dimensional chemical transport model (3D-CTM) study of N_2O fractionation, *McLinden et al.* [2003] found that YM97 cross sections "arbitrarily" scaled by a factor of two yielded a much better agreement with atmospheric measurements and with simulations using *ab initio* cross sections [*Johnson et al.*, 2001]. The need for this scaling is explained by the model outlined here, which also shows that the shape and, in certain spectral regions, the *sign* of the fractionation is poorly predicted by YM97 or scaled versions thereof. We therefore turn next to a comparison of the predictions of a zonally averaged two-dimensional (2D) trace gas model [*Shia et al.*, 1989; YM97].

[18] Briefly, the model contains 18 equally spaced latitude boxes from pole-to-pole and 40 equally spaced vertical layers in log pressure up to 0.01 mbar. The continuity equation is solved for all important, long-lived species. Transport fields above the 250 mb pressure level are tested against MLS data [*Eluszkiewicz et al.*, 1996], optimization below 250 mb uses a suite of tropospheric tracers [*Brown*, 1993]. Well tested parameterizations [*Allen and Frederick*, 1982] of the O_2 Schumann-Runge Bands (SRB, 175-205 nm) are used to calculate the N_2O photolysis rates, and all gas phase reactions in the NASA "standard" stratospheric chemistry recommendations [*DeMore et al.*, 1997] are included.

[19] The model is first run for 13 years with monthly climatological and radiation updates using the standard chemistry to simulate the total N_2O in the atmosphere, independent of isotopic effects. A standard mixing ratio of 3.1×10^{-7} for N_2O at all levels is used to start the run. The predicted N_2O vertical abundance profiles averaged over the last five years of the run are checked against monthly ATMOS profiles [*Gunson et al.*, 1990] in 10° latitudinal bins; the agreement is quantitative up to 1 mbar ($\sim$48 km).

[20] Following these tests of the transport fields and chemistry, a second 13 year run is done, this time including all singly-substituted isotopologues of N_2O ($^{15}N^{14}N^{16}O$ = 546, $^{14}N^{15}N^{16}O$ = 456, $^{14}N^{14}N^{17}O$ = 447, $^{14}N^{14}N^{18}O$ = 448), with rates for non-photolytic destruction and production for the minor isotopologues taken from the initial run. Only the photolytic cross-sections for each isotopologue are allowed to vary, fractionation in the $N_2O + O(^1D)$ reaction is ignored since the measured effects are substantially less than those for photolysis [*Johnston et al.*, 1995] and since photo-oxidation represents only a fraction ($\sim$10%) of the *total* stratospheric N_2O loss. Thanks to the sparse sampling of present atmospheric data, comparisons are made to both the mass spectrometric and limb sounding measurements of stratospheric N_2O since, while the limb sounding results are less precise, they sample a much wider range of N_2O abundances and so form a stringent test of the photolysis cross sections. Photo-oxidation is relatively more important in the lower stratosphere, and more detailed studies of the altitude dependence of ^{15}N and ^{18}O fractionation should be able to quantitatively address the relative importance of these competing loss processes [*Kaiser et al.*, 2002].

[21] Figure 3 presents the results using the photolytic fractionation factors of YM97, *Johnson et al.* [2001] and those of this work as compared to the weighted average of the available atmospheric observations whose relative values mimic the laboratory data. Model results are averaged over the last 5 years and the time periods and latitude/altitude bands of each observation. The model and observational determinations of the enrichment factors both calculate the isotopic composition of N_2O vs. $ln(f)$, where f is the fraction of N_2O remaining in the atmosphere relative to the tropospheric mixing ratio over a range of $ln(f) = -0.3 \rightarrow -4.0$ (or $\sim$150 $-$1 mbar atmospheric pressure). The observational weighted average utilizes the error bars originally reported. As Figure 3 shows, the results for the YM97 cross sections follow the *pattern* of enrichments between the various isotopologues, but are less than half those observed, similar to the laboratory discrepancies (Figure 2). Cross-sections calculated by *Johnson et al.* [2001] do a much better job of matching observational data with the particular exception of the 546 isotopologue, for which the predictions are even smaller than those of YM97 – likely due to the fixed N–N distance in the best *ab initio* PES available for N_2O.

[22] Just as is true for the laboratory results, however, the enrichment factors predicted using the cross-sections calculated with the simple but rigorous (within the Born-Oppenheimer approximation) analytical approach presented here provide a good match to the observational data and with the results of *McLinden et al.* [2003]. The agreement between the available laboratory fractionation data, physically mean-

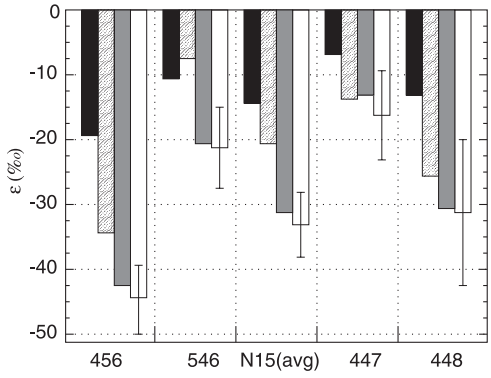

Figure 3. A comparison of the predictions of the Caltech 2D atmospheric chemistry model with the available stratospheric measurements. Isotopologues are designated by the convention used in text; N15(avg, permil) = $(\varepsilon_{456} + \varepsilon_{546})/2$. The white bars (with 2σ errors) are the weighted average of the enrichment factors from mass spectrometry of collected samples and high resolution infrared limb sounding. The black bars present the predicted enrichments using the YM97 cross sections, the bars with diagonal striping depict those using the cross sections of *Johnson et al.* [2001]. The grey bars utilize the formalism presented here.

ingful models of photolysis, and the results of stratospheric simulations provide strong evidence that the "standard" models of the atmospheric chemistry of N_2O are largely correct. The MIF ^{17}O signature in N_2O [*Cliff and Thiemens*, 1997] has been used to argue otherwise, but we stress, as do McLinden *et al*., that N_2O photolysis does not strictly follow the mass dependent $ln(1 + \delta_{447})/ln(1 + \delta_{448}) = 0.515$ relationship. The predicted MIF are consistent with the observed upper limits at 193 nm [*Röckmann et al.*, 2001a], but could be as large as a few tenths of a permil for $\lambda \gtrsim 205$ nm. While this would only account for ~half of the MIF signal observed in the atmosphere, it reduces the amount of nitrous oxide that must be produced via chemistry involving other species such as NO_2 or O_3 to ~1–2% of the global budget, a value that can be safely neglected in most mass balance calculations. Indeed, the major uncertainties in the cycling of N_2O now reside within the biosphere, and a better understanding of its production and consumption in soils and in the ocean is needed before the promise of stable isotopes in the analysis of nitrogen biogeochemistry can be realized.

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